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Rare metals preparation by electro-reduction of solid compounds in high-temperature molten salts

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Abstract Direct electro-reduction of solid compounds in molten salts is a simple and straightforward electrolytic metallurgical method, which outperforms traditional pyrometallurgical methods such as carbothermic and metallothermic reductions in terms of economic viability, energy efficiency and carbon footprint. To better highlight the features of the direct electro-reduction of solid compounds in molten salts in extraction of rare metals, the scope of this paper is focused on the know-how of the cathodic process of the direct electro-reduction of solid compounds in molten salts in extraction of rare refractory metals including Ti, Zr, Hf, V, Nb, Ta, Mo and W, and rare disperse metals including Ga and Ge. In line with an introduction of the basic concept of the method, the characteristics of reaction paths in different systems are summarized and the corresponding strategy on tailoring energy efficiency and microstructure of electrolytic products are rationalized. The economic competence of the method might be enhanced by extending the method to controllable production of rare metals with high added values, well-defined microstructure and intriguing functionality.

Keywords Rare metals; Molten salt electrolysis; Solid compounds; Electrochemical metallurgy

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1 Introduction

The present industrial extraction of metals, semimetals and alloys is through various pyrometallurgical methods [1]. Among an assortment of reductants, abundant and easily obtainable carbon-based materials are the most common reductant being used. Consequently, the carbothermic methods are predominant in the industrial extraction of iron/steel and silicon [1]. In addition, various carbon-based substances including charcoal, coal, wood and coke are mixed with iron oxides or silica at high temperatures (2000 °C for iron extraction and 1700–1900 °C for silicon extraction) to produce molten elemental iron or silicon. During the course, carbon, either in an elemental state or as carbon monoxide, functions as energy carriers to transfer precursory oxides to elements. Regardless of their environmental impact, the carbothermic methods have strong economic viability mainly due to the low cost of the energy carriers (carbon). Natural carbon-based substances generally contain some fraction of sulfur which tends to deteriorate produce or environment. The carbothermic methods operated under very high temperatures require large amounts of additional energy to compensate for the huge heat losses at high temperatures. Consequently, the energy efficiency of carbothermic methods is not high.

Metallothermic reductions using metal oxides or halides as feedstock and more reactive metals such as alkali, alkaline earth metals and aluminum as reductants are also a general route to prepare metals and semimetals in industry, including Ti, Zr, Ta, Nb, Cr and Mo [1]. The carbon emission level of metallothermic reductions themselves is satisfactory. The problem with metallothermic reductions is that the use of an alkali or alkaline earth metal greatly increases the cost of extraction because it is necessary to

perform two reaction stages: the generation of the reductants and the reduction of the metal oxides or halides. The inferior economic viability of the metallothermic route imposes constraints on the output and prevents large-scale applications of the generated metals. This issue occurs with titanium production, which is extracted using the Kroll Process involving the reduction of $TiCl_4$ by magnesium. Titanium prepared from metallothermic reduction ($8000 per ton of sponge from the Kroll Process) is far more expensive than steel ($150 per ton of steel from carbothermic reduction), which restricts the applications of Ti or Ti-based alloys in large-scale applications even though they show superior mechanical, biomedical and physicochemical properties.

In comparison with carbon and metals, electrons with adjustable activities and easy availability are ideal energy carriers for metallurgical processes. Therefore, electrochemical preparation is a promising alternative for traditional pyrometallurgical methods. Generally, availability of cost-effective and carbon-free electricity is crucial for the economic viability and the environmental benignity of an electrochemical process. At present, electricity generated from sources using less carbon or no carbon, such as nuclear power, hydroelectric power and wind power, is available and covers a fairly large fraction of generated electricity in the present grid. It is also expected that the installed capacities of electricity from nuclear power and wind power shall increase in the near-term, while the utilization of other carbon-free sources such as solar and geothermal energy shall increase in the mid- or long-term. The chemical activities of carbon and metals can only be enhanced by increasing the reaction temperatures, which consequently raises the production costs of carbothermic and metallothermic reductions, since reinforced reactor materials are required for reductions occurring at a higher temperature. In contrast, the chemical activities of electrons can be easily and delicately altered by tuning the potentials of electrodes [2].

Electrons with tunable chemical activities should be versatile energy carriers for metal extractions. In practical electrolysis, however, the chemical activities of electrons are limited by the electrochemical windows of the employed electrolytes. The narrow electrochemical windows of aqueous electrolytes restrict their applications for extracting metals whose formation voltages are higher than those of decomposition of aqueous solutions. The formation of dendrites of dissolved precursors during electrodeposition processes in aqueous solutions is another drawback in aqueous electrolytes. Owing to these disadvantages, inorganic molten salts, whose decomposition voltages are much larger than those of aqueous solutions, have come under consideration.

The electrochemical synthesis using inorganic molten salts as electrolytes achieved great success in industrial aluminum extraction, namely Hall–Héroult process [3]. In Hall–Héroult process, alumina dissolves in molten cryolite (Na_3AlF_6) and aluminum fluoride (AlF_3). The operational temperature of the electrochemical cells is around 950–980 °C. The reaction temperature is lower than those of metallothermic or carbothermic reductions, suggesting that the Hall–Héroult process is more energy-efficient. Importantly, the Hall–Héroult cell can be self-heated, with the Joule heat derived from the IR drops being adequate to sustain the high temperature of the cell. Solar thermal systems can be connected with the melt cell to maintain the melt cell holding high temperature. During electrolysis, the dissolved Al^{3+} cations are electro-reduced at cathode with formation of liquid aluminum metal. The Hall–Héroult process possesses a strong economic viability and high energy efficiency. It is also acknowledged that the huge carbon emissions remain a major shortcoming of Hall–Héroult process with utilization of carbon anodes.

The Hall–Héroult process features dissolved feedstock and liquid products. However, for metals electrodeposited in solid states, it is very difficult to effectively produce a coherent metallic deposit from molten salts, especially where dendritic depositions occur. The electrodeposition process using dissolved feedstock also suffers from the electrochemical redox reactions of shuttling couples which decrease the current efficiency and increase the energy consumption. Such a shuttling effect is the main barriers for the electrolysis of $TiCl_4$ dissolved in molten chlorides on Ti extraction.

Solid ores are the most straightforward and affordable feedstock for large-scale metallurgical process. Direct electro-reduction of solid compounds in high-temperature molten salts emerges as a novel and generic electrochemical metallurgical method, which is regarded as an innovation on refractory metal production. Its proof-of-concept was firstly demonstrated by researchers from Cambridge University as direct electro-reduction of solid TiO_2 into Ti sponges in molten $CaCl_2$ [4]. During electro-deoxidation of solid oxides in molten $CaCl_2$, oxygen ions consistently exist in the melts. Therefore, the decomposition of the molten $CaCl_2$ under cathodic polarizations is determined by the decomposition of CaO. As can be seen in Fig. 1 [5], except for some rare earth metal oxides, the decomposition potentials of most of oxides are lower than that of the molten $CaCl_2$. Under voltages lower than those of decomposition of molten salts, solid oxides (cathodes) are directly electro-reduced into solid metals at temperature lower than the melting points of both oxides and metals, with oxygen ions from oxides dissolving into electrolytes and finally discharging in anodes. Particularly, both oxides
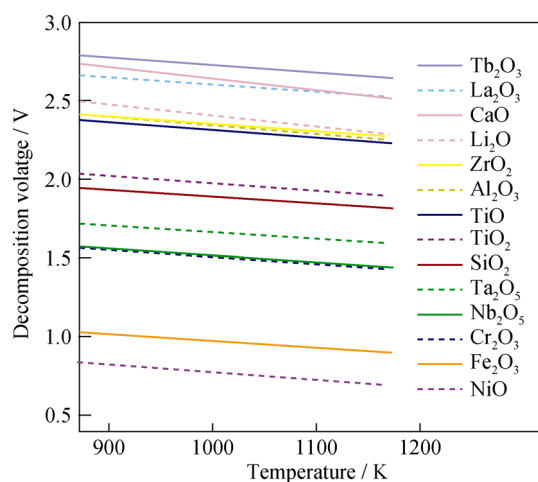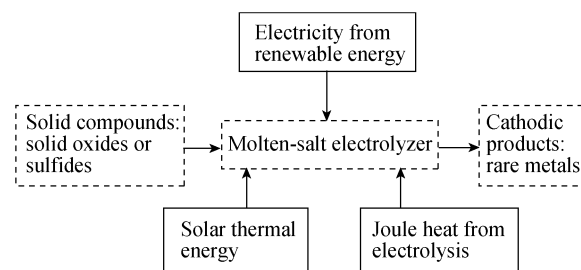
Fig. 1 Thermodynamic data on decomposition voltages of typical solid oxides in high temperatures. Adapted with permission of The Royal Society of Chemistry

Fig. 2 Schematic illustration on direct electro-reduction of solid compounds for preparation of solid rare metals

and metals show minor solubility in molten salts and mainly stand as solid states in molten salts. Therefore, the overall reaction in cathode can be expressed as Reaction (1) with M representing metals [6].

$$MO_x(s) + 2xe^- \rightarrow M(s) + xO^{2-} \qquad (1)$$
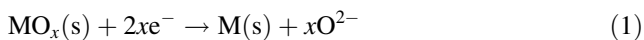
This process provides simple, short-process and potentially energy-efficient preparation of refractory metals. Compared with pyrometallurgical methods, this process occurs at much lower temperatures. The solid-to-solid reaction pathway avoids formation of dendritic electrolytic products. However, the reduction rate and space–time yield of the method is limited by the solid-to-solid mechanism due to the sluggish solid reaction kinetics. It is well documented that the mass transfer coefficient in liquid is several orders of magnitude higher than that in solid. Even in optimized conditions, the current efficiency for electrolysis of solid TiO_2 to solid Ti in molten $CaCl_2$ is less than 50 % [7], much lower than that of the Hall–Héroult process exhibiting a current efficiency higher than 90 %. This barrier causes inadequate economic competence of the method and therefore significantly retards the commercial applications of the process, despite its great success in laboratory-scale study. On the one hand, comprehensive and deep insights into the reaction mechanisms are urgently needed, which is the prerequisite for further optimizing the process. On the other hand, extension of this method for preparation of materials with high added values might compromise its demerits in sluggish kinetics. In this context, direct electro-reduction of solid compounds in high-temperature molten salts for preparation of rare metals is promising (Fig. 2), which in turn draws enormous attentions from both academic and industrial communities.

Typically, a rare metal is a rare, naturally occurring metallic chemical element of high economic value, which is regarded as strategic assets. The big family of rare metals can roughly be divided into five types: rare light metals (Li, Rb, Sc and Be), rare refractory metals (Ti, Zr, Hf, V, Nb, Ta, Mo and W), rare disperse metals (Ga, In, Tl, Ge, Se and Te), rare earth metals (Sc, Y and lanthanide) and rare radioactive metals. For rare light metals, their high chemical activity results in formation potentials comparable to that of decomposition of molten salts. Therefore, they can hardly be prepared by the studied method. Extraction of rare earth metals can be fulfilled by molten electrolysis of their solid oxides. The decomposition voltage of molten salts is comparable to those of many oxides. Therefore, there remains a debate on the contribution from the two thermodynamically favorable mechanisms, viz. electrometallothermic reduction (namely the OS process) [8–10] and direct electro-deoxidation. Direct electro-reduction of solid compounds in high-temperature molten salts is also successful in extraction of rare radioactive metals, which is regarded as an important method for processing of spent nuclear fuels. Such a topic was recently reviewed by Choi and Jeong [11].

To better highlight the features of the direct electro-reduction of solid compounds in molten salts for extraction of rare metals, this paper is focused on the know-how of cathodic process of the direct electro-reduction of solid compounds in molten salts for extraction of rare refractory metals including Ti, Zr, Hf, V, Nb, Ta, Mo and W, and rare disperse metals including Ga and Ge. The basic concepts of the direct electro-reduction of solid compounds in molten salts were well documented by previous high-quality reviews [5, 12, 13], which is briefly introduced in the initial part of the paper. At present, the practical utilization of inert anodes in the process (especially in molten chlorides) still remains a high challenge. Therefore, the detailed discussion of anodic process falls out of the range of the paper, which, however, was reviewed by a book chapter [14].

2 Ti, Zr and Hf

Titanium and its alloys have a wide variety of applications because of its lightweight, high strength, excellent resistance to corrosion and high-temperature oxidization. However, although titanium is the 9th richest resources in the earth crust, it is still regarded as a rare metal. The main reason lies in the high cost of the multiple-step pyrometallurgical production method, namely the Kroll Process, which consumes energy as high as 45–55 kWh per kg Ti sponge.

The electrochemical mechanism for direct electro-reduction of solid TiO_2 to Ti in molten $CaCl_2$ was firstly proposed as follows [4]. Upon applying a cathodic potential to a bulky TiO_2 electrode, a small amount of oxygen is removed from solid TiO_2, which is an effective insulator. The removal of a small amount of oxygen from TiO_2 results in the formation of highly conducting Magnelli phases (TiO_{2-x}), causing the bulky oxide electrode to become an electrically conducting electrode. The charge transfer reaction then occurs at the interface between the newly generated conducting oxide and molten salt, resulting in the formation of oxygen ions. Simultaneously, the oxygen anions dissolve in the molten $CaCl_2$, where they quickly diffuse out of the bulky oxides into the melt and eventually discharge at the anode. The rate-limiting step is assumed to be the diffusion of the oxygen in the solid phases. Based on the above assumption, the electro-reduction at moderate overpotentials of bulky oxides incapable of forming oxygen–metal solutions or accommodating effective oxygen diffusive kinetics through metals should feature extremely sluggish kinetics or no reaction at all. This contradicts with the fairly fast kinetics of electro-reduction reported for solid chromium oxide pellets and silicon dioxide to Cr and Si, respectively, under moderate overpotentials [6, 15]. Both Si and Cr cannot form oxygen solutions. However, Cr_2O_3 pellets with a mass of 2.5 g can be fully electro-metalized in 6 h at 2.8 V in molten $CaCl_2$ at 950 °C [6], and the W–SiO_2 electrode can be electro-reduced to Si at a reaction rate of higher than 80 A·cm^{-2} [15]. It is well known that diffusion in a liquid is generally several orders of magnitude faster than that in a solid [2]. Thus, it is more rational to conclude that oxygen diffusion in the liquid phase is the rate-determining step of electro-reduction of bulky solid oxides.

In fact, it was shown that a TiO_2 pellet with a porosity of 23 % still possessed an unreduced core after electrolysis at 3.2 V for 5 h while a TiO_2 pellet with a porosity of 68 % was fully electro-reduced after electrolysis at 3.2 V for 3 h, although the mass of feedstock in both pellets remained the same [16]. The vast difference in reduction rate for pellets with different porosities suggests the critical role of precursory porosities of bulky oxides and the dominance of oxygen diffusion in liquid.
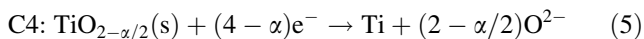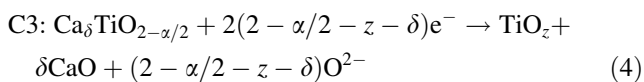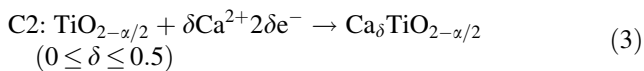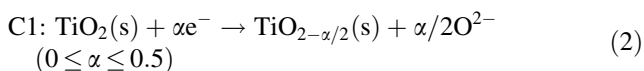
By considering the diffusion polarizations of oxygen ions in liquid and ohmic polarizations of solid cathode, three-phase interlines (3PI) models were proposed to address the kinetics of direct electro-reduction of solid oxides in molten salts, which was verified to be in good agreement with the electro-reduction of solid SiO_2 to Si [17]. This mechanism is valid as the general kinetic model governing the direct electro-reduction of solid compounds (the second type electrode process). As to the reduction of a bulky MO_x electrode in molten $CaCl_2$, direct electro-reduction of insulating MO_x starts at the initial current collector/solid MO_x/molten $CaCl_2$·3PIs. The reduction-generated M, which has a reasonable electrical conductivity, is porous due to the decrease in molar volume from MO_x to M. Simultaneously, molten $CaCl_2$ enters the pores, leading to the formation of new M/MO_x/$CaCl_2$ 3PIs which propagate along the surface of, and also penetrate into, the solid MO_x until the reduction is completed. The O^{2-} moves into the neighboring electrolyte in the reduction-generated porous M layer, and is then transported to the bulk electrolyte and finally discharge at anode. This model indicates that the reduction of bulk solid oxides (Reaction (1)) is governed by the diffusion polarizations of oxygen ions in liquid and ohmic polarizations of solid cathode.

Electro-reduction of solid TiO_2 in molten $CaCl_2$ is a multiple-step and complicated process, as confirmed by the corresponding cyclic voltammetric (CV) plot [7, 17]. As shown in Fig. 3 [5], the electro-reduction of solid TiO_2 experiences four steps [5]: formation of low-valence Ti–O (Peak C1), formation of perovskite via the electro-inclusion of Ca^{2+} from electrolytes into low-valence Ti–O (Peak C2), electrochemical reduction of perovskite to Ti–O (Peak
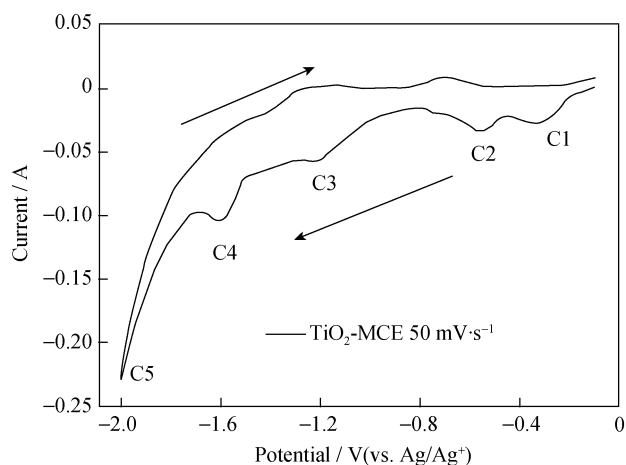
Fig. 3 A typical CV plot of TiO_2 powder loaded metallic (Mo) cavity electrode (MCE) in molten $CaCl_2$ at 850 °C recorded at 50 mV·s^{-1}. Adapted with permission of the Royal Society of Chemistry

C3) and further reduction of low-valence Ti–O to metallic Ti (Peak C4).

$$C1: TiO_2(s) + \alpha e^- \rightarrow TiO_{2-\alpha/2}(s) + \alpha/2 O^{2-}$$
$$(0 \leq \alpha \leq 0.5) \quad (2)$$

$$C2: TiO_{2-\alpha/2} + \delta Ca^{2+} 2\delta e^- \rightarrow Ca_\delta TiO_{2-\alpha/2}$$
$$(0 \leq \delta \leq 0.5) \quad (3)$$

$$C3: Ca_\delta TiO_{2-\alpha/2} + 2(2 - \alpha/2 - z - \delta)e^- \rightarrow TiO_z +$$
$$\delta CaO + (2 - \alpha/2 - z - \delta)O^{2-} \quad (4)$$

$$C4: TiO_{2-\alpha/2}(s) + (4 - \alpha)e^- \rightarrow Ti + (2 - \alpha/2)O^{2-} \quad (5)$$

With combination of the 3PI models and the above electro-reduction paths of solid TiO_2, optimization of the titanium oxide cathode for higher energy efficiency can be rationalized. As indicated, various perovskite phases often present in the partially reduced cathode, which have larger molar volume than the Ti–O phases. Moreover, the perovskite phases are thermodynamically more stable than the Ti–O phases and require more negative potential to get reduced. Therefore, it may retard the reduction and cause low energy efficiency. Such negative effects from the in situ perovskitization can be mostly avoided by ex-situ "perovskitization," in which solid $CaTiO_3$ instead of TiO_2 are employed as the cathode. It was found that the time for electrolysis of porous $CaTiO_3$ was much shorter, leading to almost a double increase in current efficiency without compromising the product quality [7].

Increasing the porosity of TiO_2 cathode is an effective protocol to enhance energy efficiency of Ti extraction. An optimal current efficiency of 54 % was recently achieved by a recyclable NH_4HCO_3 as the green additive to increase the porosity of the TiO_2 precursors. Incomplete reduction of TiO_2 pellets with low porosity (<44 %) occurred. With the porosity of TiO_2 pellets increasing to 58 %, the complete reduction with formation of pure titanium metal appeared. The optimal porosity of the TiO_2 pellet was 68 %, rendering low oxygen content in Ti, high current efficiency of 54 % and low energy consumption of 20 kWh per kg Ti [16].

The present alloy production methods used in industry are based on a two-step process involving extraction of each component and a subsequent alloying process. This process is tedious and costly. Moreover, some alloys are difficult to generate, if not impossible, because of the vast differences in the densities and melting points of each element. The above disadvantage can be overcome by the direct electro-reduction of solid mixtures in molten salts which is a one-step solid-to-solid process and capable of producing alloys of most metals without melting them. Importantly, it has been demonstrated that the reduction

potentials of oxides in alloy extraction become lower than those in individual metal extractions [18, 19]. This is because that the energy released from alloy formation is naturally exploited in the electro-reduction process to lower the electrolysis voltage. This energy is usually wasted if individual metals are extracted separately and then melted together to form the alloy. Moreover, the initially generated metal dispersed through the whole pellet not only improves the electrical conductivity of the whole cathode but also facilitates the formation of more 3PIs. This suggests that the first generated metal can function as a depolarizer to enhance the fast electro-reduction of other oxides. The merit was demonstrated by an investigation on the extraction of TiNi alloy from electrolysis of mixed oxides in molten $CaCl_2$ [19]. It was found that the cell voltage for TiNi generation was lower than that for Ti formation.

Preparation of Ti-based materials with intriguing functionality is another strategy to further enhance the economic competence of molten salt electrolysis. In line with the merit on energy efficiency, Ti–Fe alloys with applicable hydrogen storage capabilities were successfully prepared by direct electro-reduction of solid ilmenite in molten $CaCl_2$ [18].

Ti, Zr and Hf are all Group IVA elements in the periodic table, and direct reduction of their solid oxides to metals follows very similar pathways. Controllable preparation of alpha- and beta-phase TiZr alloys was achieved by electro-reduction of a solid TiO_2–ZrO_2 mixture in molten $CaCl_2$. Oxygen content in the alloys was found to play an important role in determining the phase, in which oxygen is phase-transition inhibitor from the high-temperature beta-TiZr to the low-temperature alpha-TiZr. By simply varying the electrolysis duration, phase-tunable TiZr preparation was successful [20]. Zirconium based AB_2-type hydrogen storage alloys can also be prepared by direct electrochemical reduction of their mixed oxides in molten $CaCl_2$ [21]. Particularly, the electrolytic Zr-based alloys were unique for their high initial capacities for hydrogen storage without any pre-treatment for activation.

It should be noted that Ti and Zr tend to sinter at high temperatures. Such a sintering effect leads to formation of interconnected electrolytic samples, e.g., sponge-like Ti. This causes decreased porosity in cathode during electrolysis and inferior energy efficiency of the electrolysis. However, such a sintering effect offers opportunities for near-net-shape production of electrolytic materials with well-defined geometries. Zr has a small neutron absorption cross section, and most of Zr is used as fuel cladding tubes in nuclear reactors. Direct electro-reduction of solid oxide preforms to consolidated Zr-based tubes with the maintaining of the precursory geometrical shapes was reported

as a direct, energy saving and near-net-shape production of Zr tubes [22]. Near-net-shape electrolytic Ti–6Al–4V was also reported by molten salt electrolysis of solid oxides in molten chlorides [23].

Electrolytic Ti–Si [24], Ti_2CO_n [25], HfC [26], Hf and Hf–Nb [27], Ni–35Ti–15Hf [28], NiTi shape memory alloys [29], 89Nb–10Hf–1Ti [30], Ti–15 wt% Mo [31], Ti–W [32], and TiNb [33] were also successfully demonstrated by direct electro-reduction of solid oxides in molten chlorides.

3 V, Nb and Ta

Group VA metals including V, Nb and Ta are also typical refractory metals, which are therefore suitable for production by direct electro-reduction of solid oxides in molten salts. Nb and Ta are widely used due to strong corrosion resistance, high melting points, good ductility and heat conductivity. Their major use is to prepare dielectric capacitors and superconductors. At present, most of Nb and Ta metals are commercially produced by sodiothermic reduction or aluminothermic reduction. Alternatively, direct electro-reduction of solid oxides in molten salts offers a simple and affordable preparation of Nb and Ta [34, 35].

Direct electro-reduction of solid Nb_2O_5 and Ta_2O_5 exhibits similar pathways to those of TiO_2 and ZrO_2. Figure 4 shows the typical CV plots of Nb_2O_5 powders in molten $CaCl_2$ at 900 °C [35]. Peaks c3 and c4 that only appear in the first cycle are ascribed to formation of Ca–Nb–O perovskite due to electrochemical inclusion of Ca^{2+} into solid Nb_2O_5. Peak c2 is assigned to formation of low valence of Nb–O from solid Nb_2O_5 and Ca–Nb–O perovskite. The solid oxide cathode gets full metallization at more negative potentials, resulting in occurrence of Peak
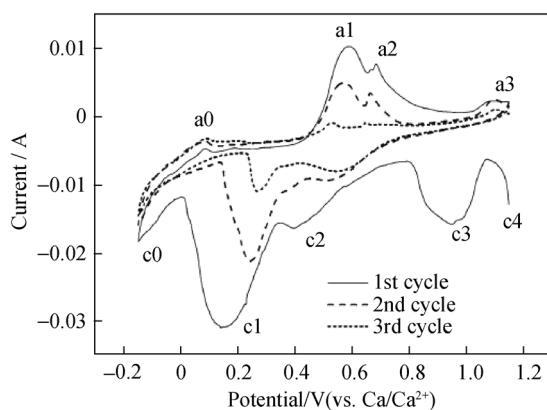
Fig. 4 Typical CV plots of Nb_2O_5 powder loaded metallic (Mo) cavity electrode (MCE) in molten $CaCl_2$ at 900 °C recorded at 20 mV·s^{-1}. Adapted with permission from PCCP Owner Societies

c1. The cathodic Peak c0 is assigned to deposition of the Ca or Ca-based alloys from molten salts. Under optimal conditions, the electrolytic Nb is prepared with a current efficiency of 50 % and energy consumption as low as 6.03 kWh per kg Nb.

Compared to Group IVA metals (Ti, Zr and Hf), the formation potentials of Group VA metals (V, Nb and Ta) are much more positive [12]. This means electrolytic V, Nb and Ta with the absence of Ca deposition resulting in enhanced energy efficiency. Such an enhancement is highlighted in electrolytic Ta from direct electro-reduction of solid Ta_2O_5 in molten $CaCl_2$, in which current efficiency and energy consumption are, respectively, 78 % and 2.4 kWh per kg Ta [34]. Nb and Ta possess much higher melting points than those of Ti and Zr [12]. Such a high melting points could effectively restrain sintering effects and agglomeration of the metal particles. Therefore, less interconnected nanoparticles of Ta and Nb were formed [34, 35].

Electrolytic V [36], Hf–Nb [27], 89Nb–10Hf–1Ti [30], TiNb and Nb_3Sn [33], V–C [37], Ti–6Al–4V [23], and NbSi [38] were also successfully demonstrated by direct electro-reduction of solid oxides in molten chlorides.

4 Mo and W

Mo and W are also typical refractory metals, with melting points being comparable to that of Nb and Ta and higher than that of Ti and Zr. Such materials are industrially produced by hydrogen reduction or metallothermic reduction methods, which cannot directly produce ultrafine products. Thermodynamically, formation potentials of Mo and W from oxides are more positive than those of Ti, Zr, Nb and Ta. Therefore, direct electro-reduction of solid oxides in molten salts is expected to offer a direct, simple and energy-efficient preparation of Mo and W. Owing to their extremely high melting points, sintering effects become less effective, helpful to formation of nanostructured electrolytic W and Mo. However, the oxides of Mo and W are either soluble or unstable in molten salts, which provoke the electrolytic Mo and W by direct electro-reduction solid compounds other than oxides in molten salts [39–44]. Therefore, the direct electro-reduction of solid compounds in molten chlorides is a promising alternative to the state of the art hydrogen reduction or metallothermic reduction for W and Mo production in terms of energy efficiency, economic competence and added values of products.

Wolframite ((Fe/Mn)WO_4) and scheelite ($CaWO_4$) are the most abundant and straightforward W ores in the earth crust. Since solid $CaWO_4$ shows minor solubility and high stability in molten chlorides, solid $CaWO_4$ instead of tungsten oxides are employed as precursory cathode for W

extraction [42–44]. A typical CV plot of solid $CaWO_4$ in molten $CaCl_2$–NaCl (equal molar ratio) at 750 °C is shown in Ref. [42]. At more positive potential, the direct electro-reduction of solid $CaWO_4$ to solid W occurs, with simultaneous oxygen and calcium removal (Reaction (6)). At more negative potentials, the in situ generated CaO gets electro-reduced into liquid Ca. It was also found that the solubility of solid $CaWO_4$ in the melts sharply increases at temperatures of higher than 750 °C. A protocol on more efficient electrolytic extraction of fine tungsten powder was demonstrated by utilizing electrolysis of solid $CaWO_4$ at 750 °C for 10 h followed by a simple washing process in the same melt but at 850 °C for 1 h. Compared to the consecutive electrolysis at 750 °C for 24 h, the proposed strategy shows double current efficiency and half energy consumption without compromise in the quality of electrolytic W. At such an optimal condition, W powders with size of 200 nm were produced at current efficiency of 54.56 % and energy consumption of 5 kWh per kg W [42].

$$CaWO_4(s) + 6e^- \rightarrow W(s) + Ca^{2+} + 4O^{2-} \quad (6)$$
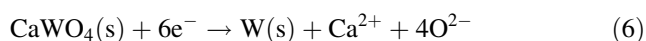
The sulfides of W and Mo are insoluble and stable in molten chlorides, which can be potential precursors for electrolytic W and Mo in molten chlorides. Intriguingly, such metal sulfides are thermodynamically less stable than the oxide counterparts. Therefore, enhanced energy efficiency is expected in direct electro-reduction of metal sulfides in molten salts.

In line with the characterizations of the electrolytic products, the direct electro-reduction path of solid MoS_2 in molten $CaCl_2$ at 850 °C was specified as the formation of solid Mo_3S_4 as the intermediate [40]. Upon electrolysis at more positive potentials, intermediated solid Mo_3S_4 is generated due to the partial electro-desulfidation of solid MoS_2 (Reaction (7)). At more negative potential, the intermediated Mo_3S_4 is further electro-reduced to Mo, resulting in the full metallization (Reaction (8)). Current efficiency of higher than 80 % was observed in the process for extraction of Mo nanopowders. The ionized sulfur can dissolve in the melt and then transferred to the graphite anode. Thermodynamically, sulfur shows much lower reactivity with carbon than that of oxygen. The ionized sulfur discharges in graphite anode, resulting in formation of elemental sulfur. The resulting electrochemical splitting of solid MoS_2 in molten chlorides with the utilization of carbon anode provides a short, no-carbon-footprint, inter-anode-enable and high-efficiency preparation of nanostructured Mo powders [40].

$$6MoS_2(s) + 8e^- \rightarrow 2Mo_3S_4(s) + 4S^{2-} \quad (7)$$

$$Mo_3S_4(s) + 8e^- \rightarrow 3Mo(s) + 4S^{2-} \quad (8)$$
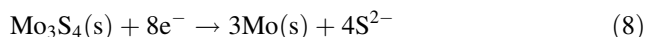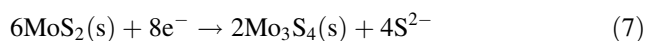
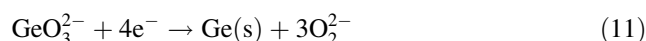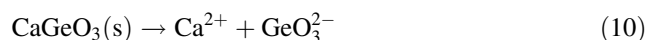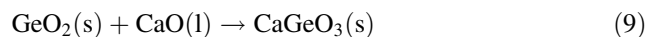Direct electro-splitting solid MoS_2 into Mo and elemental sulfur was also fulfilled and optimized in

molten NaCl–KCl at 700 °C [41]. Owing to the lower temperature, the energy efficiency is further enhanced. Under optimal conditions, Mo nanoparticles with size ranging from 50 to 100 nm were prepared at a current efficiency of as high as 92 % and energy consumption of as low as 2 kWh per kg Mo [41]. In the same melts, ultrafine W powders with size ranging from 50 to 100 nm were prepared by direct electro-splitting solid WS_2 with current efficiency and energy consumption, respectively, of >90 % and 1.23 kWh per kg W [39]. The electro-splitting of solid metal sulfides was successfully extended to copper extraction by electro-splitting solid copper sulfide in molten $CaCl_2$–NaCl at 800 °C [45].

5 Ga and Ge

Ga and Ge are rare disperse metals, which are important functional materials. Ferromagnetic Ni_2MnGa alloys were successfully prepared by direct electro-reduction of mixed oxides (NiO, MnO_2, and Ga_2O_3) in molten $CaCl_2$, in which the stoichiometry of the products was consistent with that in the precursors [46].

Direct electro-reduction of solid oxides for preparation of Si and Ge were demonstrated, in which the electrolytic Si and Ge are nanowires or nanoparticles [47–54]. Since Si and Ge are semimetal or even nonmetal. Therefore, the aggregation of Si and Ge particles is restrained in molten salts. The solid-to-solid reaction mechanism cannot address the formation of nanowires of Si and Ge, which, however, can be interpreted by the in situ dissolution–electrodeposition mechanism [49]. The coexisted solid-to-solid mechanism and the dissolution–electrodeposition mechanism during the course of electro-reduction of solid SiO_2 to solid Si in molten $CaCl_2$ are schematically illustrated in Fig. 5 [49].

The dissolution–electrodeposition mechanism is also present during the electro-reduction of solid GeO_2 to solid Ge in molten $CaCl_2$. Upon electrolysis of solid GeO_2 in molten chlorides, the concentration of O^{2-} in the electrochemical interface is high, which triggers the formation of $CaGeO_3$ in cathode (Reaction (9)). The in situ generated $CaGeO_3$ then dissolves in molten chlorides (Reaction (10)), and solid Ge is consequently produced through the electrodeposition of the dissolved germanates (Reaction (11)) [47, 52].

$$GeO_2(s) + CaO(l) \rightarrow CaGeO_3(s) \quad (9)$$

$$CaGeO_3(s) \rightarrow Ca^{2+} + GeO_3^{2-} \quad (10)$$

$$GeO_3^{2-} + 4e^- \rightarrow Ge(s) + 3O_2^{2-} \quad (11)$$

The above verified dissolution–electrodeposition is in line with the observed intermediates of silicates or germanates
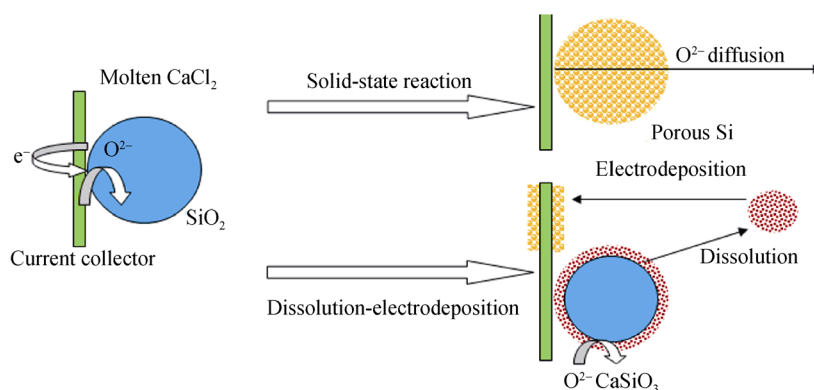
Fig. 5 Schematic illustration on coexisted solid-to-solid mechanism and dissolution–electrodeposition mechanism during course of electro-reduction of solid SiO_2 to solid Si in molten $CaCl_2$. Adapted with permission of The Royal Society of Chemistry
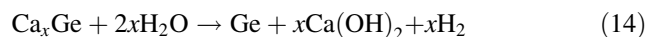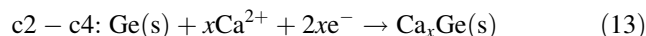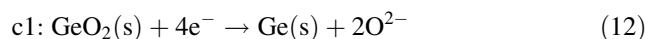
during the electro-reduction of solid SiO_2 or GeO_2 in molten chlorides [47–54]. This not only enlarges the fundamental understanding on the molten salt electrolysis of solid compounds but also provides a reasonable explanation on the formation of nanostructured Si and Ge. The electrodeposited Ge can function as nucleation centers for the growth of Ge generated from solid feedstock. At low overpotentials, the generation amount of nuclei is few, facilitating anisotropic growth of Ge and resulting in formation of Ge nanowires. At high overpotentials, the present abundant nuclei lead to the formation of low-aspect-ratio products, namely nanoparticles [47, 52]. Therefore, direct electrochemical reduction of solid GeO_2 offers a simple, affordable controllable and scalable production of nanostructured Ge. Considering the intriguing functionality of nanostructured Ge, the electrolytic Ge possesses high economic competence.

Figure 6 [51] displays a typical CV plot of solid GeO_2 in molten $CaCl_2$–NaCl at 600 °C. The cathodic Peak c1 is assigned to formation of Ge (Reaction (12)). At more negative potentials, three pairs of reversible peaks appear. The corresponding cathodic peaks (c2–c4) are due to the formation of Ca–Ge alloys in different stoichiometry (Reaction (13)). In particular, Ca species can be facilely removed from Ca–Ge by rinsing Ca–Ge in water at room temperatures (Reaction (14)). Based on the electrochemical behavior of solid GeO_2 in molten chlorides and chemistry between water and Ca–Ge, the controllable preparation of nanoporous Ge via an electrochemical reduction–alloying process in molten salt (reduction and alloying) and post-zero-energy-consumption water etching (dealloying) was proposed and demonstrated [51]. During the process, solid GeO_2 is electro-reduced into nano-Ge, which is then electrochemically transformed into Ca–Ge at more negative potentials in the same melt. After the following rinse in water, nanoporous Ge is produced. As can be seen in the insets of Fig. 6, the suspensions of the prepared nanoporous Ge with different
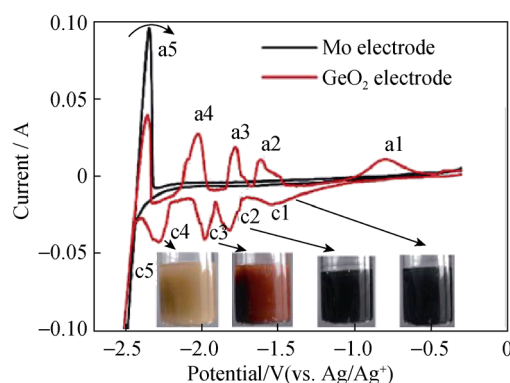
Fig. 6 Typical CV plots of GeO_2 powder loaded metallic (Mo) cavity electrode (MCE) in molten $CaCl_2$–NaCl at 600 °C recorded at 20 mV·s^{-1}. Adapted with permission of The Royal Society of Chemistry

porosity show different colors, indicating their tunable optical properties. This suggests that the direct electro-reduction of solid oxides is a controllable preparation of nanoporous functional materials.

$$c1: GeO_2(s) + 4e^- \rightarrow Ge(s) + 2O^{2-} \quad (12)$$

$$c2 - c4: Ge(s) + xCa^{2+} + 2xe^- \rightarrow Ca_xGe(s) \quad (13)$$

$$Ca_xGe + 2xH_2O \rightarrow Ge + xCa(OH)_2 + xH_2 \quad (14)$$

6 Perspective

Direct electro-reduction of solid compounds in molten salts is a simple and straightforward electrolytic metallurgical method, which outperforms traditional pyrometallurgical methods such as carbothermic and metallothermic reductions in terms of economic viability, energy efficiency and carbon footprint. Short-term large-scale deployment of the above approach in metallurgy remains a challenge, mainly due to insufficient energy efficiency, sluggish reduction

kinetics, challenges in inert anode and continuous operation. However, the inadequate economic competence of the method might be alleviated by extending the method to controllable production of rare metals with high added values and intriguing functionality. In particular, many unusual interfacial processes in the solid cathode exist in molten salt electrolysis of solid compounds, which might offer opportunities on high-efficient preparation of rare metal functional materials. It is believed that the deep and comprehensive insights into the reaction mechanism and functionality of electrolytic samples are the prerequisite on its commercialization. The development of inert anodes still remains less explored. It should be noted that the inert anodes designed for the Hall–Héroult process could also be suitable for the process. To achieve less or zero carbon emissions, the development on fabricating high performance and affordable inert anodes are highly desired. To achieve a high current efficiency and low energy consumption, cathode preform should possess a high surface/thickness ratio and a suitable porosity. This thus limits the batch yield. In addition, the configurations of current electrolytic cells are incapable of accommodating the requirement of continuous production. Thus, the innovations on designing electrolytic cells capable of achieving a high throughput and a continuous operation are needed.

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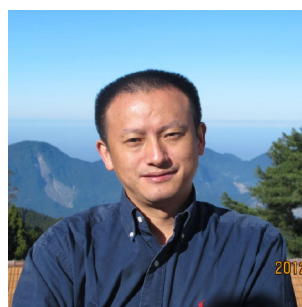
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